(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 449 685 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number : **91400614.3**

(22) Date of filing : **06.03.91**

(51) Int. Cl.[5] : **C08K 5/00**, C08L 23/02, // (C08K5/00, 5:20, 5:527, 5:13, 5:3492, 5:3435)

(30) Priority : **14.03.90 JP 64727/90**

(43) Date of publication of application : **02.10.91 Bulletin 91/40**

(84) Designated Contracting States : **CH DE FR GB IT LI NL**

(71) Applicant : **SUMITOMO CHEMICAL COMPANY, LIMITED**
5-33, Kitahama 4-chome Chuo-ku
Osaka (JP)

(72) Inventor : **Ishii, Tamaki**
1-12-2, Uchihonmachi
Suita-shi, Osaka 564 (JP)
Inventor : **Yachigo, Shinichi**
2-10-5-406, Sonehigashimachi
Toyonaka-shi, Osaka 561 (JP)

(74) Representative : **Bourgognon, Jean-Marie et al**
Cabinet Flechner 22, Avenue de Friedland
F-75008 Paris (FR)

(54) Stabilized polypropylene resin composition.

(57) A polypropylene resin containing an α-olefinic copolymer rubber and an inorganic filler is stabilized by incorporating therein the following 6 components :

(A) a hindered phenolic compound having a molecular weight of not less than 500,

(B) a high-molecular hindered piperidine compound such as poly[{6-(1,1,3,3 - tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl}{(2,2,6,6-tetramethyl-4-piperidyl)-imino}hexamethylene{(2,2,6,6-tetramethyl-4-piperidyl)-imino}],

(C) a low-molecular hindered piperidine compound such as 2-methyl-2-(2,2,6,6-tetramethyl-4-piperidyl)amino-N-(2,2,6,6-tetramethyl-4-piperidyl)-propionamide,

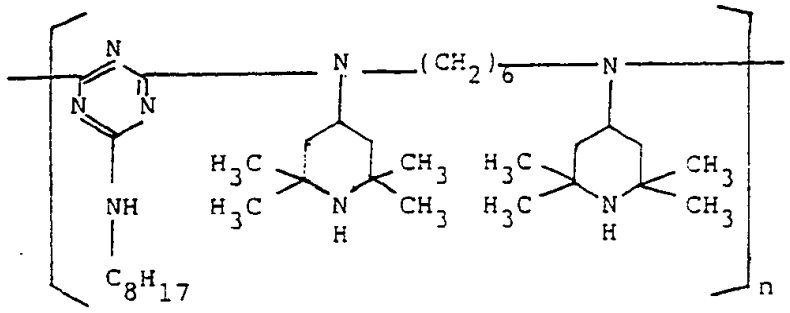
(D) a benzoate compound such as 2,4-di-t-butylphenyl 3,5-di-t-butyl-4-hydroxybenzoate,

(E) a phosphorous compound such as bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite, and

(F) an amide compound such as ethylenebisstearylamide. This composition may also contain a sulfur compound such as dialkyl thiodipropionate and pentaerythritol tetrakis(3-alkylthiopropionate). The composition disclosed is stable not only against heat and oxidation but also against light.

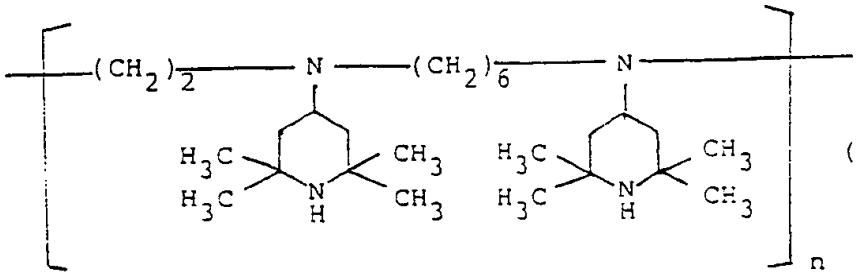
EP 0 449 685 A1

wherein n is 2 to 20,



(B - 2)

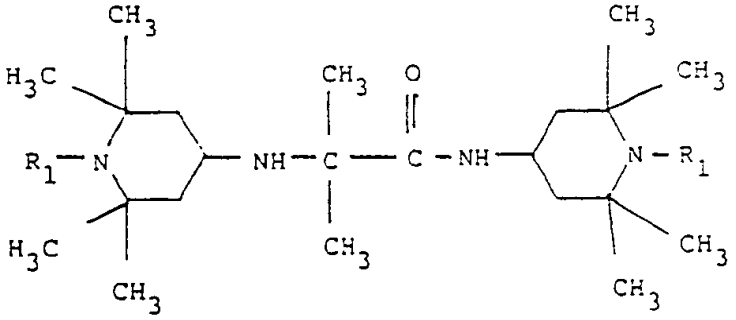
wherein n is 2 to 20,



(B - 3)

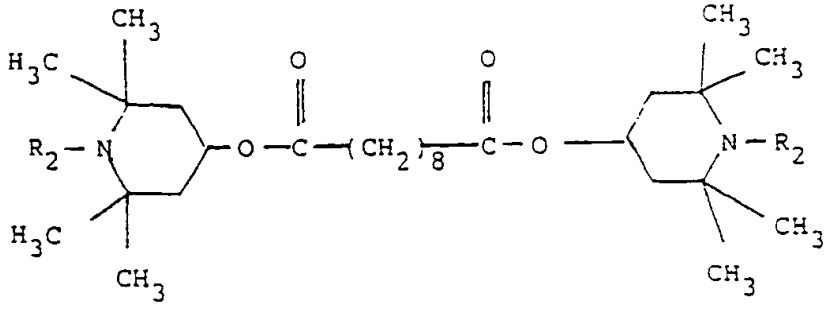
wherein n is 2 to 20;

(C) 0.01 to 1 part by weight of a low-molecular hindered piperidine compound selected from the following formulas (C - 1) and (C - 2):



(C - 1)

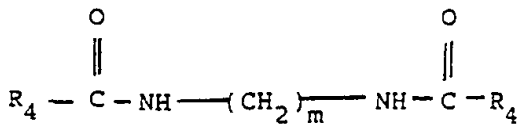
wherein R_1 is hydrogen or alkyl of 1 to 3 carbon atoms,



(C - 2)

and

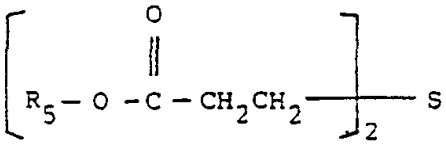
(F) 0.01 to 1 part by weight of an amide compound represented by the following pormula (F - 1);



(F - 1)

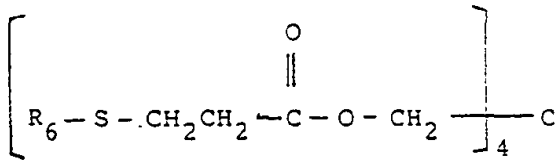
wherein R_4 is alkyl of 5 to 21 carbon atoms or alkenyl of 5 to 21 carbon atoms, and m is an integer of 1 to 6.

The present invention further provides a polypropylene resin composition which comprises, in addition to the above components (A), (B), (C), (D), (E) and (F), not more than 0.2 part by weight of a sulfur compound (G) selected from those represented by the following formulas (G - 1) and (G - 2):



(G - 1)

wherein R_5 is alkyl of 4 to 20 carbon atoms,



(G - 2)

wherein R_6 is alkyl of 4 to 20 carbon atoms.

The polypropylene which is a base component of the composition of the present invention may be a homopolymer of propylene and besides, may be copolymers containing an ethylene component in addition to the propylene as a main component, including propylene-ethylene block copolymer and block copolymer of propylene and ethylene-propylene rubber. Among them, the latter, especially block copolymers containing an ethylene component are preferred. When a copolymer containing an ethylene component is used, the ethylene component is contained usually in an amount of not more than 20% by weight based on the weight of the copolymer. The polypropylene resin mixture in the present invention contains an α-olefinic copolymer rubber and an inorganic filler in addition to the above polypropylene.

The α-olefinic copolymer rubber used in the present invention is a rubber-like polymer obtained by copolymerization of two or more α-olefins. The α-olefins which are copolymerizing components include, for example, those of 2-12 carbon atoms. Copolymer rubbers of ethylene and another α-olefin are especially preferred as the α-olefinic copolymer rubber. The α-olefins to be copolymerized with ethylene are, for example, of 3-12 carbon atoms and include, for example, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, and mixtures thereof. Among them preferred are propylene and 1-butene. When copolymer rubbers of ethylene and another α-olefin are used, ethylene content in the copolymer rubbers is preferably about 45-95% by weight, more preferably about 50-80% by weight. The α-olefinic copolymer rubbers to be used in the present invention further include those copolymerized with a third component of a straight chain or cyclic monomer having non-conjugated double bond such as 5-ethylidene-2-norbornene and dicyclopentadiene.

Amount of α-olefinic copolymer rubber blended with polypropylene resin is 5-40% by weight, preferably 5-30% by weight based on the total weight of the polypropylene resin mixture. If the amount is less than 5% by weight, the composition is inferior in impact resistance and, if it is more than 40% by weight, the composition becomes troublesome in processability, etc.

Inorganic fillers used in the present invention include, for example, talc, carbon black, titanium dioxide, zinc oxide, aluminum hydroxide, calcium carbonate, magnesium carbonate, calcium sulfate, barium sulfate, calcium silicate, magnesium silicate, micas, sellaite, kaolin, zeolite, silica, asbestos, glass fiber, carbon fiber, barium titanate, and lead titanate. These may be used each alone or in combination of two or more. These inorganic fillers preferably have an average particle size of 20 μ or less, more preferably 5 μ or less. In the present inven-

copolymer rubber and inorganic filler are 0.01-1 part by weight, preferably 0.02-0.5 part by weight of hindered phenolic compound (A), 0.01-1 part by weight, preferably 0.1-0.5 part by weight of hindered piperidine compound (B), 0.01-1 part by weight, preferably 0.1-0.5 part by weight of hindered piperidine compound (C), 0.01-1 part by weight, preferably 0.1-0.5 part by weight of benzoate compound (D), 0.01-1 part by weight, preferably 0.02-0.5 part by weight of phosphorous compound (E), and 0.01-1 part by weight, preferably 0.02-0.5 part by weight of amide compound (F). If amounts of these compounds (A), (B), (C), (D), (E) and (F) are less than 0.01 part by weight, the desired effect cannot be sufficiently exhibited, and addition of them in the amounts of more than 1 part by weight gives no further increase of effect and is economically disadvantageous.

Furthermore, according to the present invention, stability against heat, oxidation and light, especially stability against heat and oxidation can be further improved by adding a sulfur compound of (G) in addition to the compounds of (A), (B), (C), (D), (E) and (F). The sulfur compounds of (G) are represented by the aforementioned formula (G-1) or (G-2). R_5 in the formula (G-1) is alkyl of 4-20 carbon atoms and is preferably alkyl of 12-18 carbon atoms. R_6 in the formula (G-2) is alkyl of 4-20 carbon atoms and is preferably alkyl of 6-18 carbon atoms. Of these sulfur compounds of (G), those which are represented by the formula (G-2) are preferred and especially preferred are those of R_6 being alkyl of 6-18 carbon atoms.

Hitherto, it has been considered that hindered amine type light stabilizers and sulfur type antioxidants have antagonium and their combination use is not preferred. However, it has become clear by the present invention that if the sulfur compound is used in a small amount, the effect is rather improved. That is, when sulfur compound (G) is used in the present invention, an amount thereof is 0.2 part by weight or less based on 100 parts by weight of the polypropylene resin mixture containing α-olefinic copolymer rubber and inorganic filler, and excess addition thereof is not preferred because stability against light, in particular, is deteriorated. It is preferred to use the sulfur compound in an amount of at least 0.005 part by weight in order to exhibit the notable effect of using the sulfur compound. More preferred range of addition amount of the sulfur compound (G) is 0.01-0.1 part by weight based on 100 parts by weight of the polypropylene resin mixture.

As far as properties of the composition are not damaged, the polypropylene resin composition of the present invention may further contain other additives such as antioxidants, light stabilizers, metal deactivators, metallic soap, nucleating agents, lubricants, antistatic agents, flame retardants and pigments.

Any methods suitable for obtaining homogeneous compositions can be employed for blending the polypropylene resin with the α-olefinic copolymer rubber, the inorganic filler, the components (A), (B), (C), (D), (E) and (F), the optional component (G) and, other additives to be used, if necessary. That is, these components may be simultaneously blended or may be respectively blended in a plurality of steps. Furthermore, a part or all of these components may be blended as masterbatches. These components can be kneaded by usual methods, for example, using roll, Banbury mixer, single-screw extruder, twin-screw extruder, or the like.

As explained above, the present invention provides polypropylene resin compositions which have high stability against heat, oxidation and light by adding to a polypropylene resin containing an α-olefinic copolymer rubber and an inorganic filler a specific hindered phenolic compound, a specific high-molecular hindered piperidine compound, a specific low-molecular hindered piperidine compound, a specific benzoate compound, a specific phosphorous compound, and a specific amide compound, and, if necessary, a specific sulfur compound. Therefore, these polypropylene resin compositions are especially useful as materials for parts which are exposed to heat, oxygen and light in use, for example, parts of automobiles and electrical equipments.

The following nonlimiting examples will further explain the present invention.

Example 1

The components as shown in Table 1 were added to unstabilized propylene-ethylene block copolymer (ethylene content of 7.3% by weight) and they were mixed by a Henschel mixer and further kneaded and pelletized by a 30 mmø twin-screw extruder. The resulting pellets were molded into test pieces of 60 x 40 x 1 mm by a 5.5 ounce injection molding machine. These test pieces were subjected to a weathering test.

The weathering test was carried out in a Sunshine weatherometer (hereinafter referred to as "SWOM") under the conditions of a black panel temperature of 83°C and a water spray cycle of 18 min/120 min. Evaluation was effected by measuring the time before occurrence of cracks on the surface of the test piece. The results are shown in Table 1 as a life until cracking.

Separately, test pieces of 40 x 40 x 1 mm were prepared and stabilities against heat and oxidation were evaluated by measuring the time before 30% of area of the test piece embrittled in a Geer oven of 150°C. The results are shown in Table 1 as a life until embrittlement.

In this example, ethylene-propylene copolymer rubber having an ethylene content of 75% by weight was used as an α-olefinic copolymer rubber.

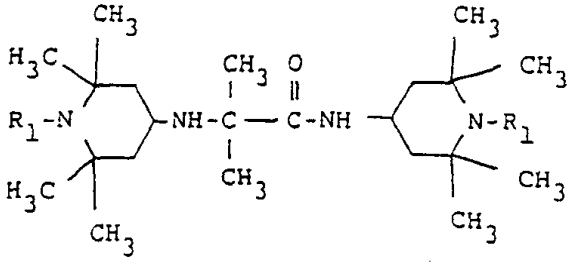
In Table 1, amounts of α-olefinic copolymer rubber and the inorganic filler are shown as % by weight based

Table 1 (1)

No.			Examples												
			1	2	3	4	5	6	7	8	9	10	11	12	13
Resin composition (% by weight)	α-olefininc copolymer rubber		25	25	25	25	25	25	25	25	25	25	25	25	25
	Inorganic fillers	Talc	10	10	10	10	10	10	10	10	10	10	10	10	10
		Carbon black													
		Glass fiber													
Additives Upper column: Kind Lower column: Part by weight	Phenolic type [(A)]		A-1 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	A-2 0.1	A-3 0.1	A-4 0.1	A-5 0.1	A-6 0.1
	Piperidine type [(B)]		B-1 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	B-2 0.2	B-3 0.2	B-2 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2
	Piperidine type [(C)]		C-1 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	C-2 0.2	C-1 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2
	Benzoate type [(D)]		D-1 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2
	Phosphorous type [(E)]		E-1 0.1	E-2 0.1	E-3 0.1	E-4 0.1	E-5 0.1	E-1 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1
	Amide type [(F)]		F-1 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1
	Sulfur type [(G)]														
Test results	Life until brittlement (hr) at 150°C		1870	1880	1850	1850	1840	1840	1880	1850	1860	1830	1840	1800	1790
	Life until cracking (hr) at 83°C in SWOM		2400	2340	2280	2280	2280	2400	2460	2220	2460	2460	2460	2420	2420

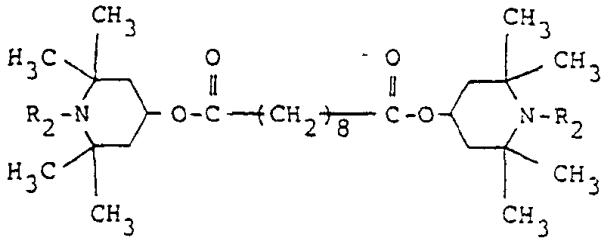
Table 1 (3)

No.			Comparative Examples											
			27	28	29	30	31	32	33	34	35	36	37	38
Resin composition (% by weight)	α-olefininc copolymer rubber		25	25	25	25	25	25	25	25	25	10	10	10
	Inorganic fillers	Talc	10	10	10	10	10	10	10	10	10	30	30	30
		Carbon black											5	
		Glass fiber												5
Additives Upper column: Kind Lower column: Part by weight	Phenolic type [(A)]		A-1 0.1	〃 0.1		A-1 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1		A-1 0.1	〃 0.1	〃 0.1
	Piperidine type [(B)]		B-2 0.2		B-2 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2		B-2 0.2	〃 0.2	〃 0.2	〃 0.2
	Piperidine type [(C)]			C-1 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2		C-1 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2
	Benzoate type [(D)]		D-1 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2		D-1 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2	〃 0.2
	Phosphorous type [(E)]		E-1 0.1	〃 0.1	〃 0.1	〃 0.1		E-1 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1
	Amide type [(F)]		F-1 0.1	〃 0.1	〃 0.1		F-1 0.1	〃 0.1	〃 0.1	〃 0.1	〃 0.1			
	Sulfur type [(G)]					G-2 0.05	〃 0.05	〃 0.05	〃 0.05	〃 0.05	〃 0.05	〃 0.05	〃 0.05	〃 0.05
Test results	Life until brittlement (hr) at 150°C		1450	980	350	1150	1520	1500	1490	1100	520	920	840	910
	Life until cracking (hr) at 83°C in SWOM		1260	1200	2160	1560	1260	1320	1140	1080	2040	1440	1020	1380



(C - 1)

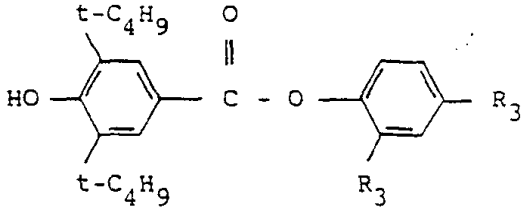
wherein R_1 is hydrogen or alkyl of 1 to 3 carbon atoms,



(C - 2)

wherein R_2 is hydrogen or alkyl of 1 to 3 carbon atoms;

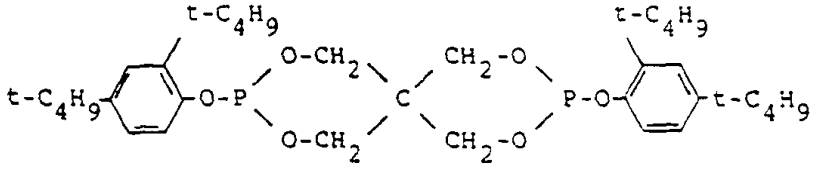
(D) 0.01 to 1 part by weight of a benzoate compound represented by the following formula (D-1):



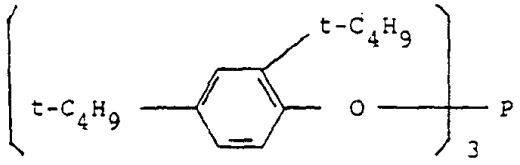
(D - 1)

wherein R_3 is t-butyl or t-amyl;

(E) 0.01 to 1 part by weight of a phosphorous compound selected from the following formulas (E-1) through (E-5):



(E - 1)



(E - 2)

wherein R_6 is alkyl of 4 to 20 carbon atoms.

3. The composition according to claim 1, wherein said α-olefinic copolymer rubber comprises a copolymer rubber of ethylene with another α-olefine having 3 to 12 carbon atoms.

4. The composition according to claim 3, wherein an ethylene content in said copolymer rubber is 45 to 95 % by weight based on the weight of the copolymer rubber.

5. The composition according to claim 1, wherein said inorganic filler is selected from talc, carbon black, titanium dioxide, zinc oxide, aluminum hydroxide, calcium carbonate, magnesium carbonate, calcium sulfate, barium sulfate, calcium silicate, magnesium silicate, micas, sellaite, kaolin, zeolite, silica, asbestos, glass fiber, carbon fiber, barium titanate and lead titanate.

6. The composition according to claim 5, wherein said inorganic filler comprises talc.

7. The composition according to claim 6, wherein said inorganic filler comprises talc and another inorganic filler.

8. The composition according to claim 7, wherein said another inorganic filler is present in an amount of 0 to 20 % by weight based on the weight of the polypropylene resin mixture.

9. The composition according to claim 1, wherein said hindered phenolic compound (A) having a molecular weight of not less than 500 is 3,9-bis[2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5·5]undecane, tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxymethyl] methane, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate,
1,3,5-tris(3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate,
1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene,
triethylene glycol bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate],
octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, bis[2-t-butyl-4-methyl-6-(3-t-butyl-5-methyl-2-hydroxybenzyl)phenyl] terephthalate, or
1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane.

10. The composition according to claim 9, wherein said hindered phenolic compound (A) having a molecular weight of not less than 500 is 3,9-bis[2-{3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5·5]undecane.

11. The composition according to claim 1, wherein said high-molecular hindered piperidine compound (B) has a repeating unit of the formula (B-1) or (B-2).

12. The composition according to claim 1, wherein said low-molecular hindered piperidine compound (C) has the formula (C-1) in which R_1 is hydrogen or methyl, or has the formula (C-2) in which R_2 is hydrogen or methyl.

13. The composition according to claim 1, wherein said benzoate compound (D) has the formula (D-1) in which R_3 is t-butyl.

14. The composition according to claim 1, wherein said phosphorous compound (E) has the formula (E-1) or (E-2).

15. The composition according to claim 1, wherein said amide compound (F) has the formula (F-1) in which R_4 is alkyl of 11 to 18 carbon atoms.

16. The composition according to claim 1, wherein said amide compound (F) is methylenebisstearylamide, ethylenebisstearylamide, ethylenebisoleylamide, or hexamethylenebisstearylamide.

17. The composition according to claim 1, which contains 0.02 to 0.5 part by weight of said hindered phenolic compound (A), 0.1 to 0.5 part by weight of said high-molecular hindered piperidine compound (B), 0.1 to 0.5 part by weight of said low-molecular hindered piperidine compound (C), 0.1 to 0.5 part by weight of

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 40 0614

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 42 (C-564)[3390], 30th January 1989; & JP-A-63 241 048 (SUMITOMO CHEM. CO., LTD) 06-10-1988 & US-A-4 985 479 (H. NAGASAKI et al.)	1-20	C 08 K 5/00 C 08 L 23/02 // (C 08 K 5/00 C 08 K 5:20 C 08 K 5:527 C 08 K 5:13 C 08 K 5:3492 C 08 K 5:343)

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 08 K
C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-05-1991	WILSON A.J.D.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)